Physical Chemistry
for Energy Engineering
(14th: 2018/11/05)

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Course schedule (as of Nov. 5)

Deadline for appealing on exam-1 result: Nov. 12
Submission time of the homework-2: beginning of the class on Nov. 12.

	29-Oct	No lecture
	31-Oct	
14	5-Nov	2. Phase equilibrium-1
15	7-Nov	2. Phase equilibrium-2
16	12-Nov	3. Chemical equilibrium-1
17	14-Nov	Answers of homework-2
18	19-Nov	Exam-02 (2 hour)
19	21-Nov	3. Chemical equilibrium-2
20	26-Nov	3. Chemical equilibrium-3
21	28-Nov	3. Chemical equilibrium-4
22	3-Dec	3. Chemical kinetics-1
23	5-Dec	3. Chemical kinetics-2
24	10-Dec	3. Chemical kinetics-3
25	12-Dec	Answers of homework-3
26	17-Dec	Exam-03 (2 hour)

Contents of today

<Last class>

2.2. Equilibrium theory: free energy

2.2.3. Maxwell relations and some useful formula

2.2.4. How to calculate thermodynamic quantities

<Today's class>

2.3. Phase equilibrium-1: a typical case (1 component)

Review of the last class
2.2.4. How to calculate thermodynamic quantities
- entropy change in phase transition ($21.3)-

We consider a case in which a phase transition is involved.

The entropy change upon the phase transition can be written as:

$$\Delta_{trs}S = \frac{q_{rev}}{T_{trs}}$$

Phase transition can be reversed by changing the temperature ever so slightly.

e.g.) melting of ice at 1 atm: the system will be all ice if *T* is slightly less than 273.15 K and all liquid if *T* is slightly greater than 273.15 K

Considering it takes place at a fixed temperature (T_{trs}) and under a constant pressure,

$$\Delta H = \Delta U + P\Delta V + \int V dP = \Delta U + P\Delta V = (q_P - P\Delta V) + P\Delta V = q_P,$$

then $\Delta_{trs}S = \frac{\Delta_{trs}H}{T_{trs}}$

*$\Delta_{trs}H$ and $\Delta_{trs}S$ are the enthalpy and the entropy for the phase transition.

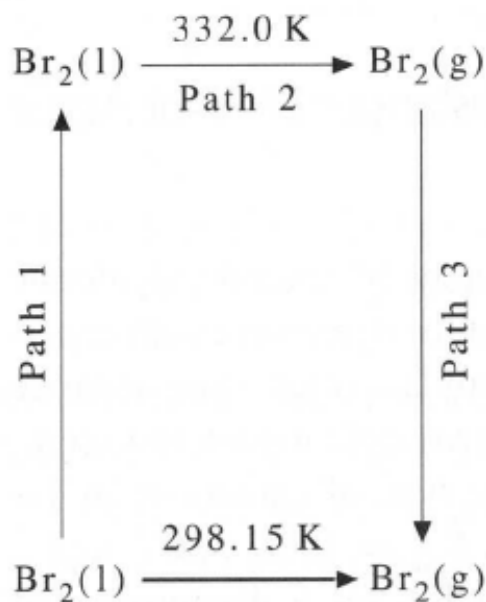*In a case in which melting is involved between 0 K and T K, for example:*

$$S(T) = \int_0^{T_{fus}} \frac{C_P^S(T)dT}{T} + \frac{\Delta_{fus}H}{T_{fus}} + \int_{T_{fus}}^T \frac{C_P^l(T')dT'}{T'}$$

(A)   (B)   (C)

*C_P^S and C_P^l are the heat capacity of the solid and the liquid, respectively.

Review of the last class
2.2.4. How to calculate thermodynamic quantities
- entropy change ($21.5)-

To calculate the standard molar entropy of $Br_2(g)$ @298.15 K.

<Here we assume the following data are known.>
- ✓ The normal boiling point of $Br_2(l)$: 332.0 K
- ✓ The standard molar entropy of $Br_2(l)$ @298.15 K:
$$\overline{S}^{\circ}_{298}[Br_2(l)] = 152.2 \text{ J K}^{-1} \text{ mol}^{-1}$$
- ✓ The molar heat capacity of $Br_2(l)$:
$$\overline{C_P^l} = 75.69 \text{ J K}^{-1} \text{ mol}^{-1}$$
- ✓ The molar heat capacity of $Br_2(g)$:
$$\overline{C_P^g} = 36.02 \text{ J K}^{-1} \text{ mol}^{-1}$$
- ✓ The molar enthalpy of vaporization at 332.0 K:
$$\Delta_{vap}\overline{H} = 29.54 \text{ kJ mol}^{-1}$$

<Path-1> $\Delta\overline{S_1} = \overline{S}^l(332.0\ K) - \overline{S}^l(298.15K) = \overline{C_P^l}\ln\frac{T_2}{T_1} = 8.140$ J K^{-1} mol^{-1}

<Path-2> $\Delta\overline{S_2} = \overline{S^g}(332.0\ K) - \overline{S}^l(332.0K) = \frac{\Delta_{vap}\overline{H}}{T_{vap}} = 88.98$ J K^{-1} mol^{-1}

<Path-3> $\Delta\overline{S_3} = \overline{S^g}(298.15\ K) - \overline{S^g}(332.0K) = \overline{C_P^g}\ln\frac{T_1}{T_2} = -3.970$ J K^{-1} mol^{-1}

<In sum> $\overline{S}^{\circ}_{298}[Br_2(g)] = \overline{S}^{\circ}_{298}[Br_2(l)] + \Delta\overline{S_1} + \Delta\overline{S_2} + \Delta\overline{S_3} = 245.5$ J K^{-1} mol^{-1}

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

Review of the last class
2.2.4. How to calculate thermodynamic quantities
- reaction entropy ($21.5)-

✓ As the same with enthalpy (i.e. standard molar enthalpy of formation), the standard molar entropies give us the entropy change by a chemical reaction.

✓ In a general case "$a\,A + b\,B \rightarrow y\,Y + z\,Z$", for example, the standard entropy change is given by:

$$\Delta_r S^0 = y \times \bar{S}^{\circ}[Y] + z \times \bar{S}^{\circ}[Z] - a \times \bar{S}^{\circ}[A] - b \times \bar{S}^{\circ}[B]$$

- -

[Example] "$H_2\,(g) + \frac{1}{2}\,O_2\,(g) \rightarrow H_2O\,(l)$", here $\bar{S}^{\circ}[H_2(g)]$=130.7 J K^{-1} mol^{-1}, $\bar{S}^{\circ}[O_2(g)]$=205.2 J K^{-1} mol^{-1}, $\bar{S}^{\circ}[H_2O(l)]$=70.0 J K^{-1} mol^{-1}.

$$\Delta_r S^0 = 1 \times 70.0 - 1 \times 130.7 - \frac{1}{2} \times 205.2 = -163.3 \text{ J K}^{-1} \text{ mol}^{-1}$$

➢ Because there is an absolute reference level for entropy thanks to the 3rd law, we do not need to consider "formation entropy".

➢ For enthalpy, because there is no unique reference level in definition, we should consider "formation enthalpy" to make "the enthalpy of the simple (elemental) substances at standard state" to be reference levels.

✓ In this chapter, we will study phase equilibria through phase diagrams.
  ➢ Phases to be treated are gas, liquid and solid. (no plasma!)
    ➢ (g): gas (or vapor), (l): liquid, (s): solid
  ➢ "Condensed phase" (condensed matter) represents liquid and solid.

✓ To draw a phase diagram, we will use a criterion of Gibbs energy:
  ➢ "a state of the lowest Gibbs energy is the most stable and thus appears as equilibrium state"
  ➢ Thus, in phase diagram (of 1 component), we fix temperature and pressure, usually. (x-axis: temperature, y-axis: pressure)

✓ In a practical condition, multiple phases generally coexist. How to coexist can be analyzed by using "chemical potential".

If we use Lennard-Jones potential, the gas behaviors similar to vdW gas.

- ✓ Ar
- ✓ Constant volume condition: $V/n = 0.025$ m³ (=25 L); 100 K
- ✓ LJ potential (with parameters given before)
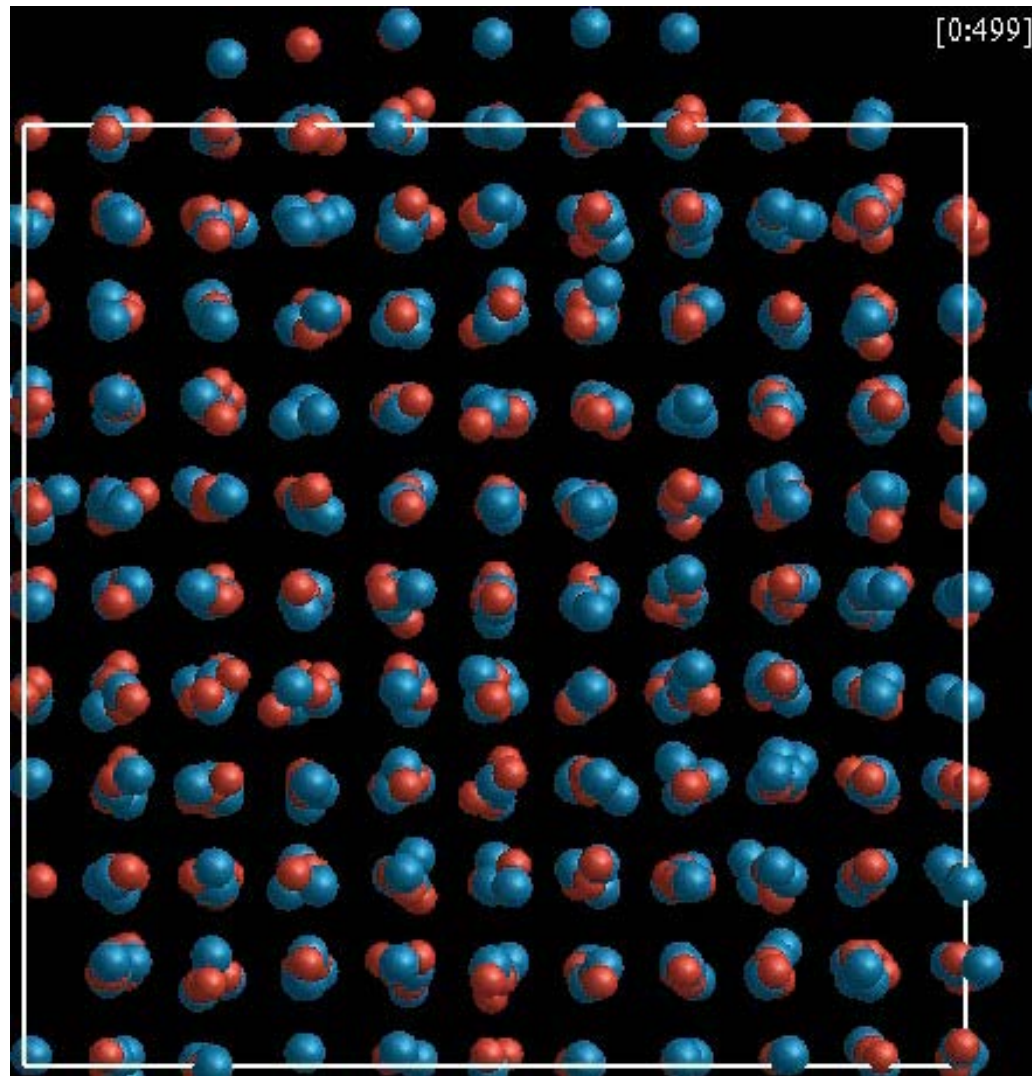
vdW gas
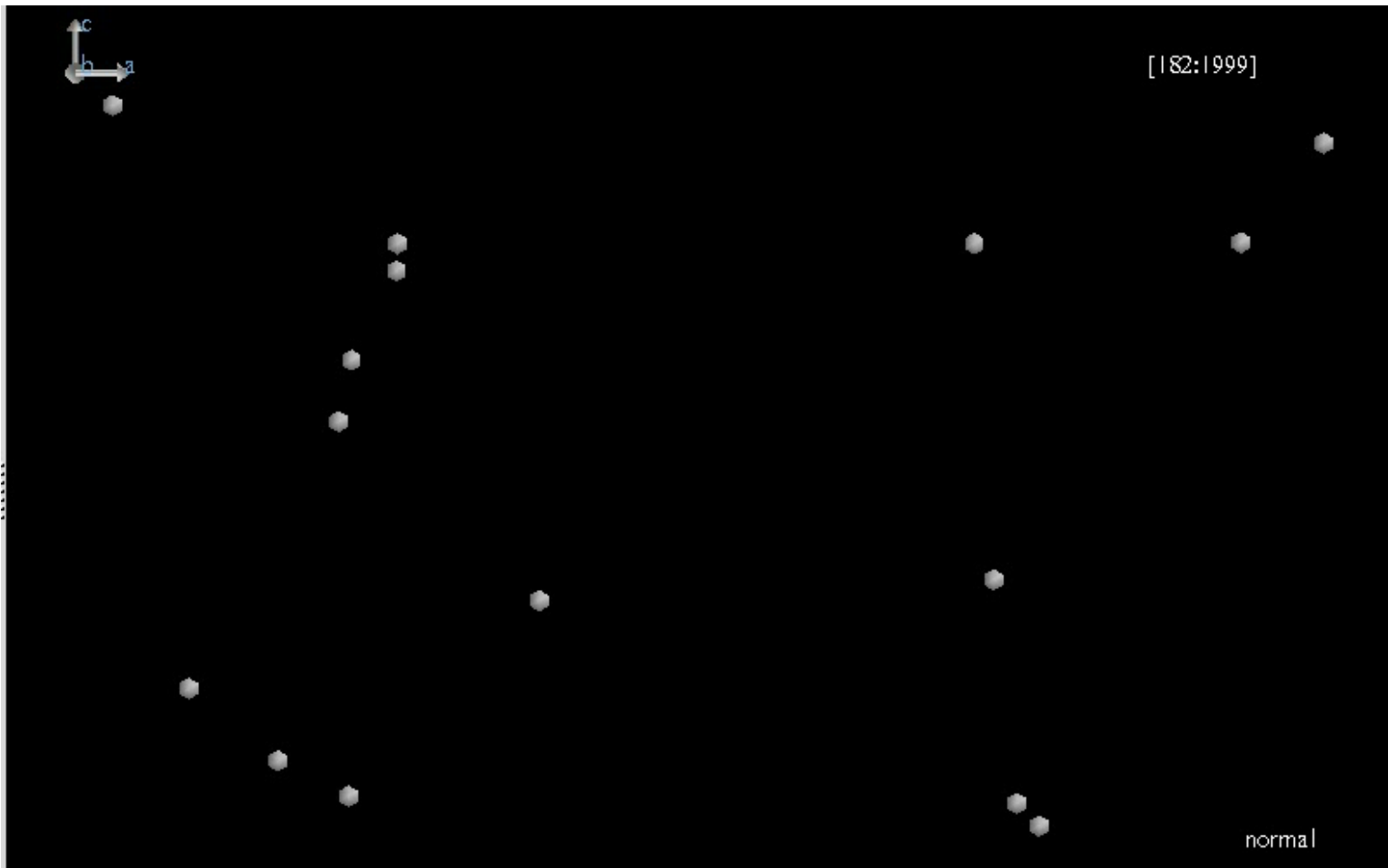
Appendix) Molecular dynamics simulation of different phase
– MgO @ 300K as a solid -

- ✓ 300 K
- ✓ Solid state

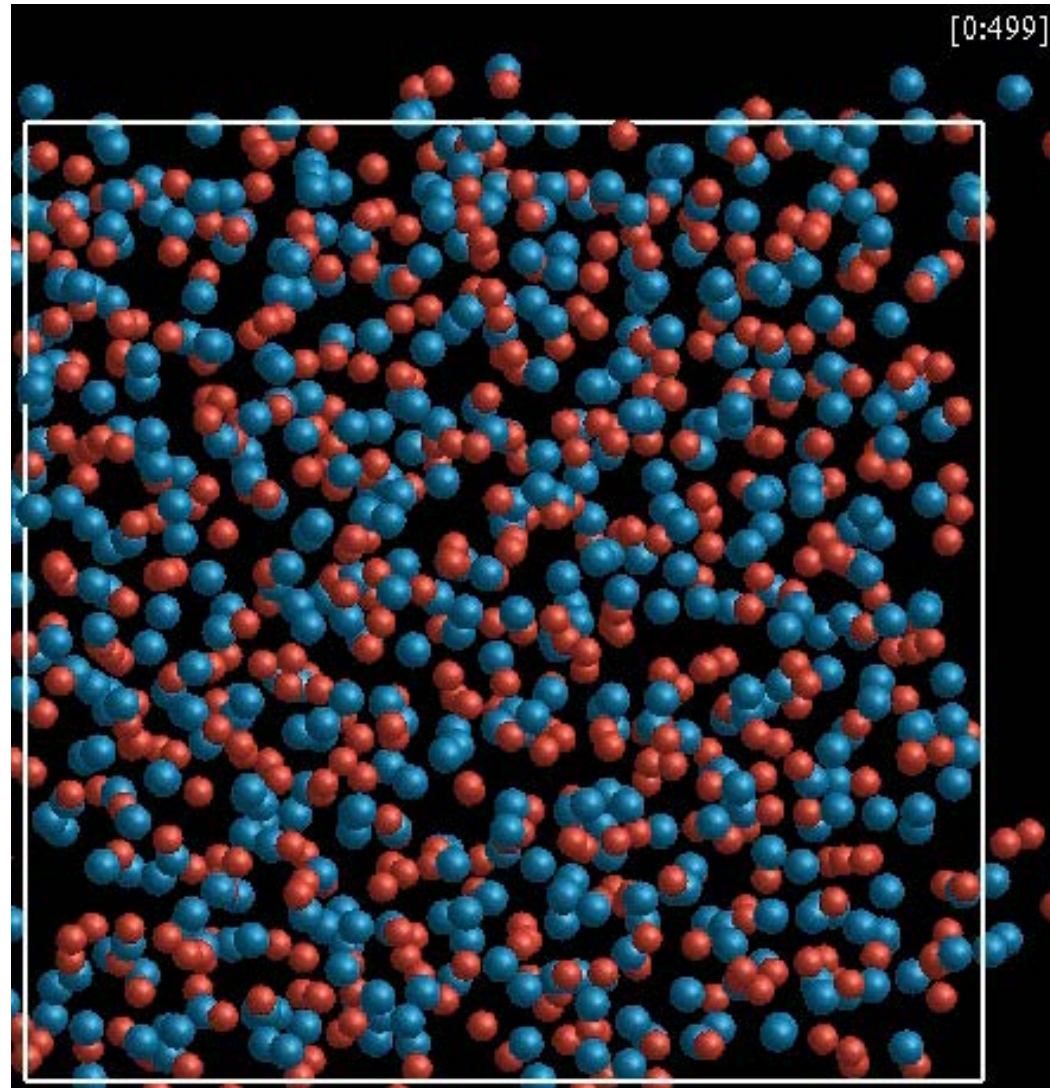- ✓ 10 fs/step
- ✓ 500 steps for 5 ps
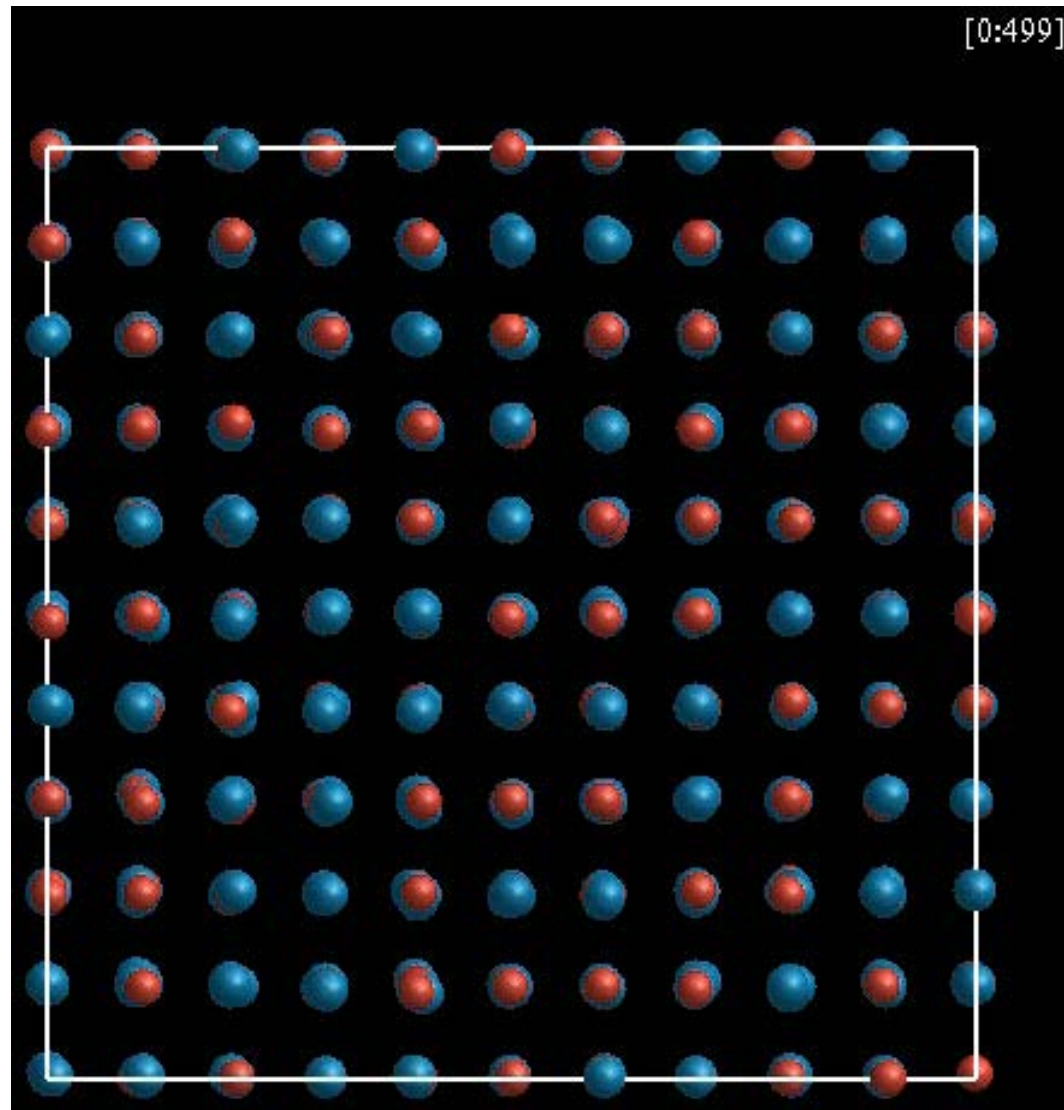
Appendix) Molecular dynamics simulation of different phase
– MgO @ 2400K as a solid -

- ✓ 2400 K
- ✓ Solid state

- ✓ 10 fs/step
- ✓ 500 steps for 5 ps

✓ 3600 K
✓ Liquid state

✓ 10 fs/step
✓ 500 steps for 5 ps

- ✓ 1800 K (cooling after melting)
- ✓ Solid state, but amorphous

- ✓ 10 fs/step
- ✓ 500 steps for 5 ps

*We do not consider this kind of solid state at 1800 K, because more ordered crystal often has a smaller Gibbs/Helmholtz energy, and the lowest free energy state is the most important in equilibrium theory.
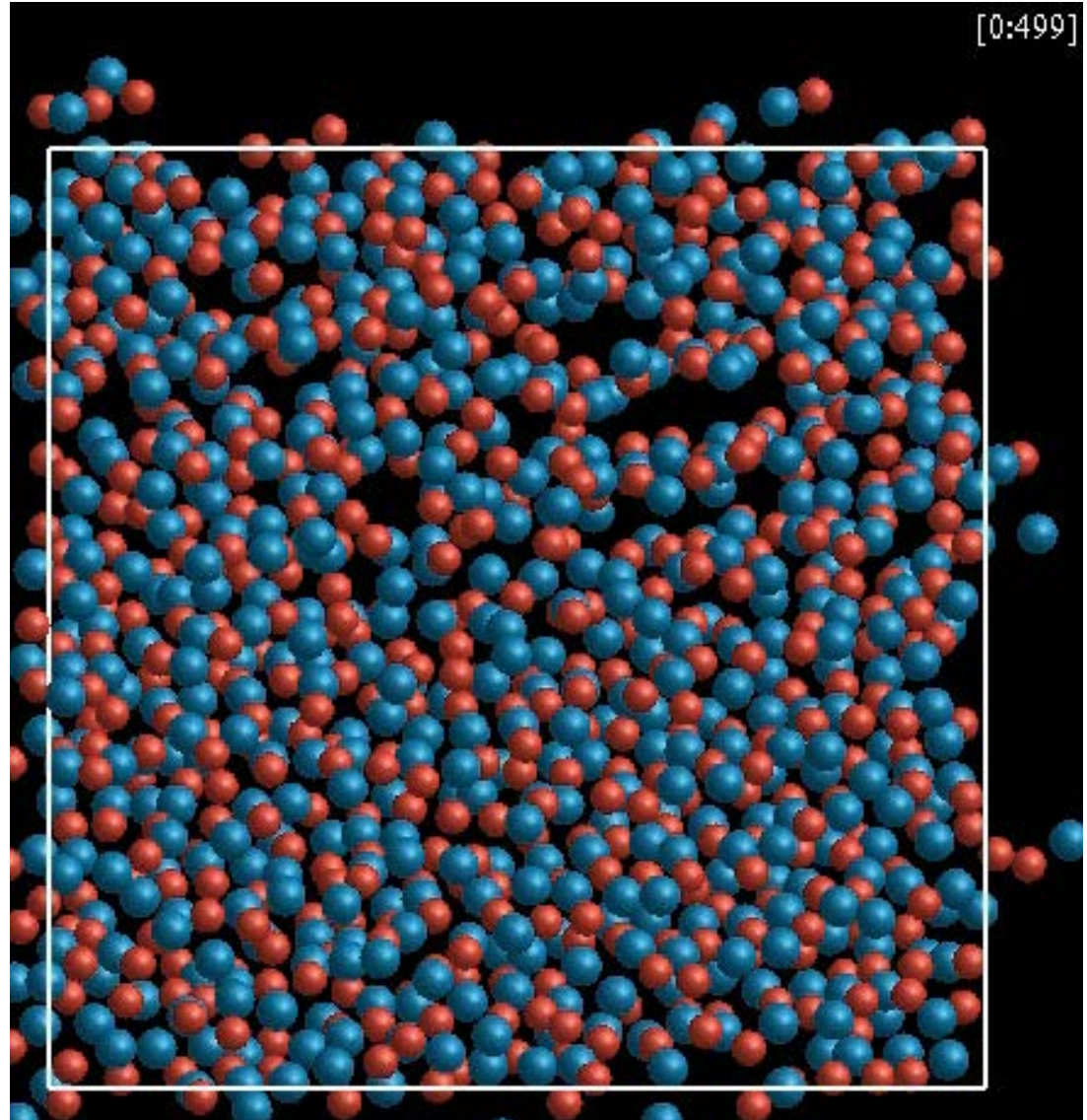
✓ Phase diagram shows "under what conditions of pressure and temperature the various states of matter of a substance exist in equilibrium".
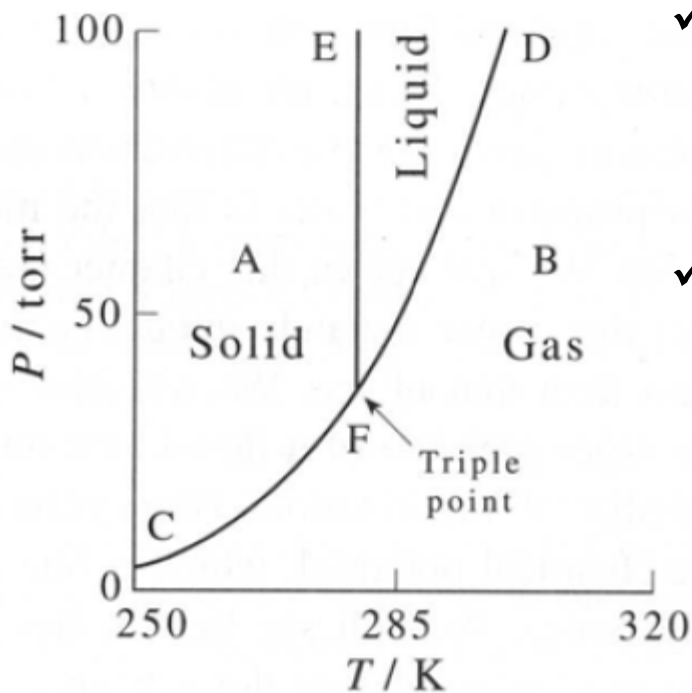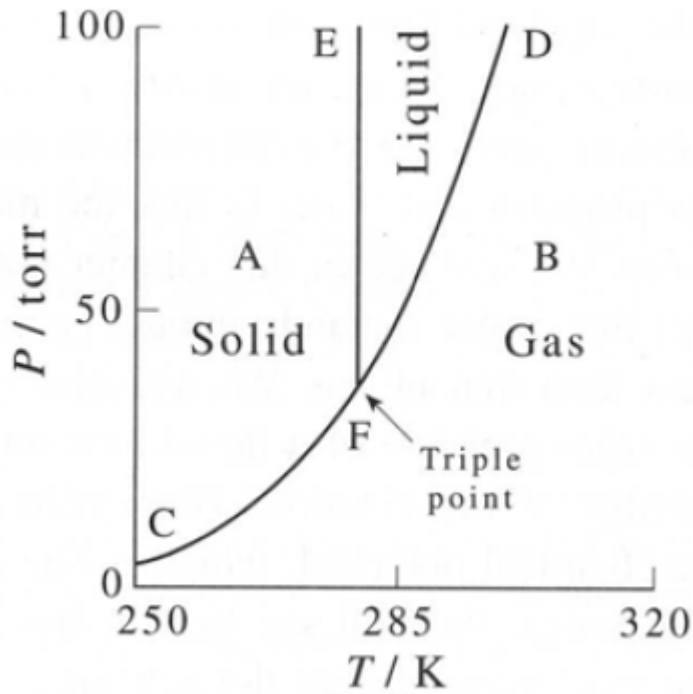

The phase diagram of benzene

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

✓ There are basically three regions: gas, liquid and solid. Within an area, a single phase exists.
  ➢ Ex-1) 50 Torr and 250 K: solid
  ➢ Ex-2) 50 Torr and 300 K: gas

✓ The separating lines indicate pressures and temperatures at which two phases coexist in equilibrium.
  ➢ C-F (b/w solid and gas; solid-gas coexistence curve): the vapor pressure of solid benzene as a function of temperature.
  ➢ F-D (b/w liquid and gas; liquid-gas coexistence curve): the vapor pressure of liquid benzene as a function of temperature
  ➢ F-E (b/w/ solid and liquid; solid-liquid coexistence curve): the melting point of benzene as a function of pressure.

Quiz

The phase diagram of benzene

*760 torr = 1 atm

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

(Quiz-1) In phase diagram, what is the definition of pressure for a phase?
- ✓ (1) the external pressure (if we consider the phase is the system)
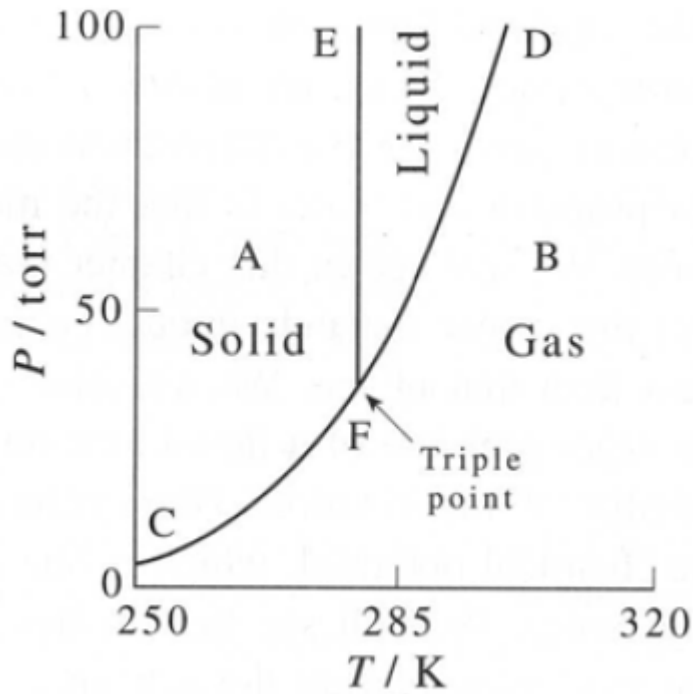- ✓ (2) the pressure of the phase.

(Quiq-2) If we have some liquid benzene in this room at 290 K, how much is the gas pressure of benzene in this room?
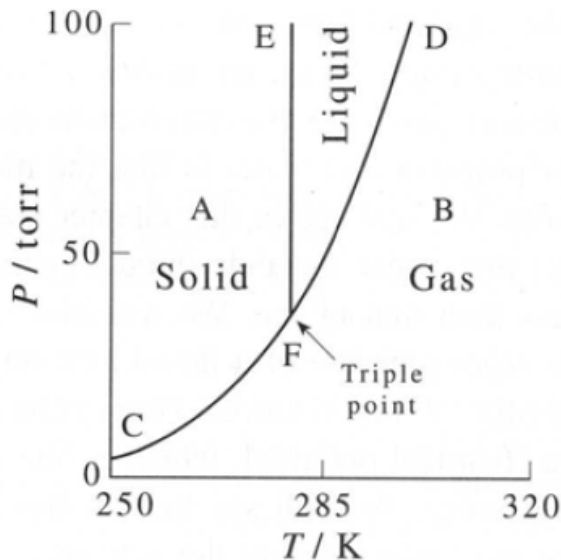- ✓ (1) ~10 torr
- ✓ (2) ~50 torr
- ✓ (3) ~100 torr

(Quiq-3) In the same condition of quiq-2, how much is the liquid pressure of benzene?
- ✓ (1) ~10 torr
- ✓ (2) ~50 torr
- ✓ (3) ~100 torr

The phase diagram of benzene

*760 torr = 1 atm

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

(Quiz-1) In phase diagram, what is the definition of pressure for a phase?
- ✓ (1) the external pressure (if we consider the phase is the system) >> O
- ✓ (2) the pressure of the phase. >> O

(Quiq-2) If we have some liquid benzene in this room at 290 K, how much is the gas pressure of benzene in this room?
- ✓ (1) ~10 torr >> ✗
- ✓ (2) ~50 torr >> O
- ✓ (3) ~100 torr >> ✗

(Quiq-3) In the same condition of quiq-2, how much is the liquid pressure of benzene?
- ✓ (1) ~10 torr >> ✗
- ✓ (2) ~50 torr >> ✗
- ✓ (3) ~100 torr >> ✗
   *The answer should be ~760 torr.

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

(Quiq-2) If we have some liquid benzene in this room at 290 K, how much is the gas pressure of benzene in this room?

>> ~50 torr

(Quiq-3) In the same condition of quiq-2, how much is the liquid pressure of benzene?

>> ~760 torr.

*760 torr = 1 atm

✓ To draw a phase diagram very practically for "usual conditions" (1 atm), we need to compare (1) the gas phase at some 50 torr and (2) liquid phase at 760 torr, and (2) check the condition when their Gibbs energies equal to find a gas-liquid equilibrium condition (at a given temperature).

✓ However, we normally consider the same pressure condition, as "thermodynamic(al) limit". This works sufficiently in "usual conditions", as
   ✓ The Gibbs energy of liquid/solid does not largely depend on pressure.
   ✓ The Gibbs energy of gas does not largely depend on the co-existence of other gasses (e.g. air). (as far as the pressure is not very high)

The phase diagram of benzene
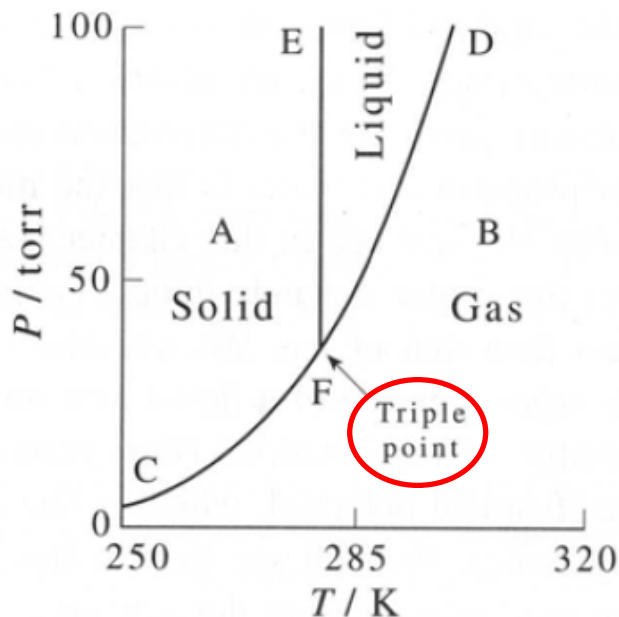
✓ The three lines intersect at one point (point F), at which solid, liquid and gaseous benzene coexist at equilibrium.
  ➢ This point is called "triple point", which is 278.7 K and 36.1 torr for benzene.
✓ If the pressure is less than that at the triple point (<36.1 torr for benzene), benzene passes directly from the solid to gaseous phase, namely *sublime* (*sublimation* as noun).

<**(Gibbs') phase rule**> The degree of freedom (of intensive properties) f is described as: $f = c - p + 2$, where c is the number of components, p is the number of phase that coexist at equilibrium at that point.
  ✓ For the phase diagram of benzene, as $c = 1$ (only benzene), $f = 3 - p$.
    ➢ Within a single-phase region, $p = 1$ thus $f = 2$. We need to give two properties (temperature & pressure, here) to specify the state.
    ➢ On a line, $p = 2$ thus $f = 1$. Thus, one intensive property is enough.
*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).
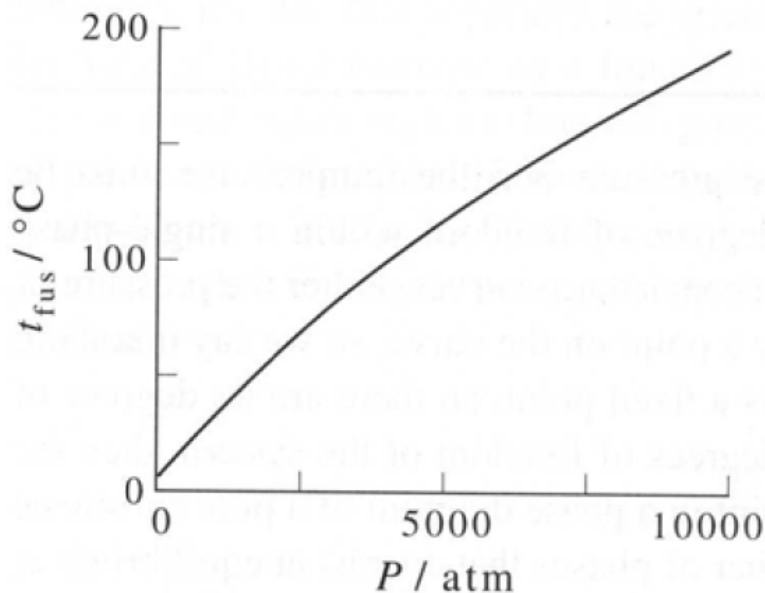
*The phase diagram
of benzene
(P is in logarithm)*
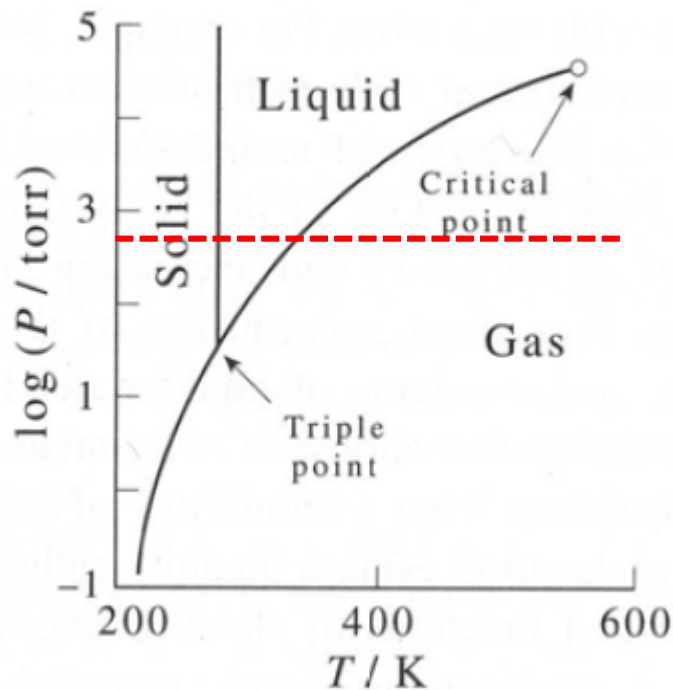
✓ If we start on the pressure axis at 760 torr (= 1 atm) and move horizontally to the right (the red broken line), we can see how benzene behaves with increasing temperature at constant pressure of 760 torr, for example.

➢ At 278.7 K, we reach the solid-liquid coexistence curve. This point is called "normal melting point" (for 1 atm).

➢ The melting point at 1 bar (1×10^5 Pa) is called "standard melting point".

*be sure that 1 atm ≠ 1 bar, although they are very close.

➢ At 353.2 K, we reach the liquid-gas coexistence curve. This point is normal boiling point.

✓ Apparently, the melting point is not sensitive to the pressure, while the boiling point is.

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

✓ At 10000 feet (3100 m) height, the atmospheric pressure is 500 torr. Then, the boiling point decreases at 340 K (from 353 K at 760 torr).

➢ Recall that the boiling point is defined to be that the temperature at which the vapor pressure equals to the atmospheric pressure.

The melting point dependence on pressure in benzene
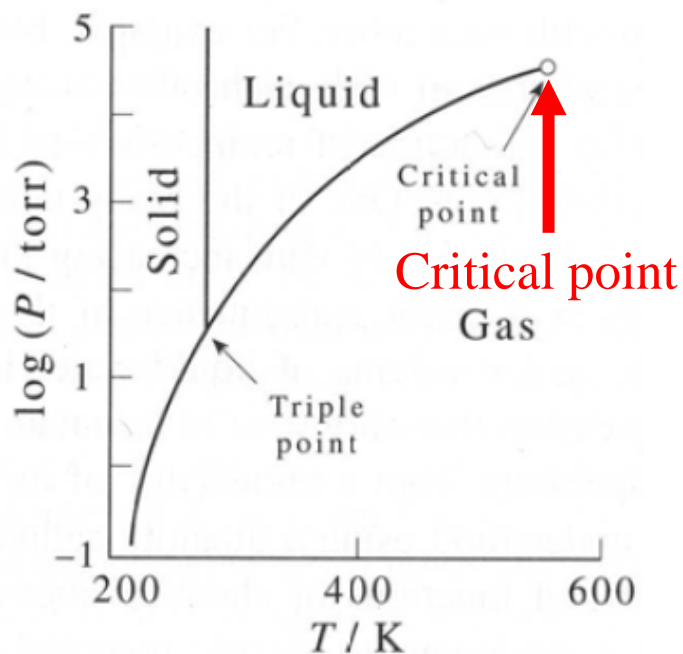
The boiling point dependence on pressure in benzene
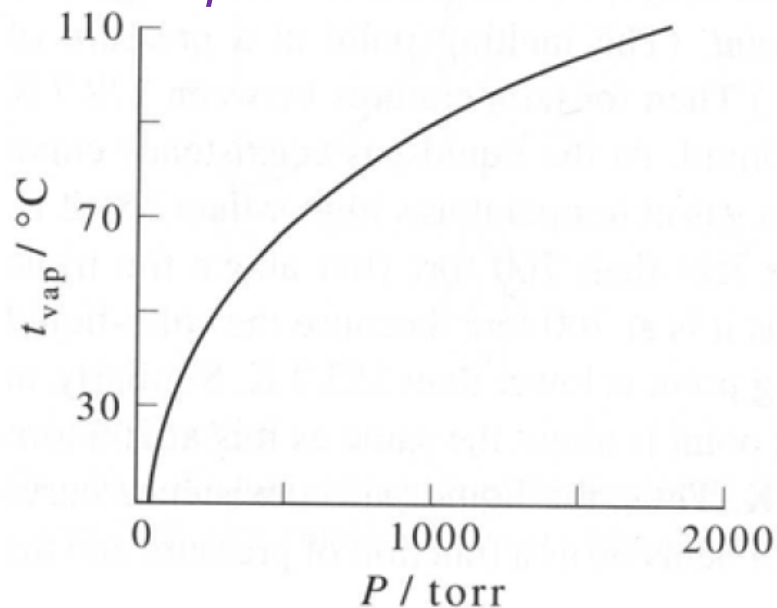
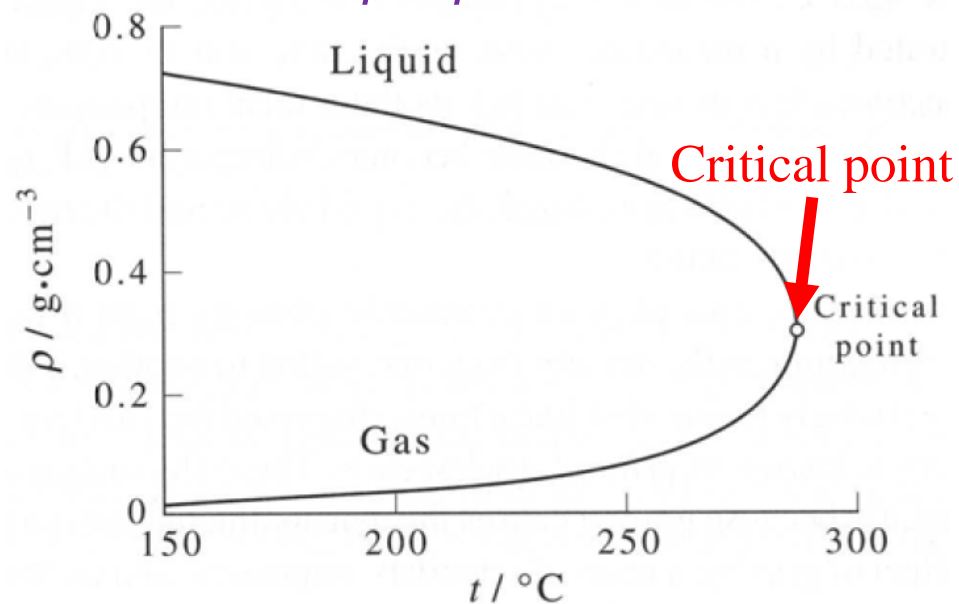*Be careful that the pressure unit is atm in the left and torr in the right. (1 atm = 760 torr)

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

The phase diagram of benzene

"Orthobaric" densities of the liquid and the vapor phase of benzene

- ✓ The liquid-gas coexistence curve ends abruptly at the critical point, where the difference between the liquid and gaseous phases are not distinct.
- ✓ If both temperature and pressure are larger than the critical point values, the liquid and the vapor phase simply merge into a single fluid phase, which is called *supercritical fluid*.
- ✓ The *orthobaric* densities, which are densities along the liquid-vapor coexistence curve, of the liquid and the gaseous phases show that these densities become equal at the critical point (right figure).

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

To supercritical state of water (increasing temperature with a constant volume)
The critical temperature of water is 374ºC.

*http://www.youtube.com/watch?v=29oy1UCHJIE

The molar enthalpy of vaporization of benzene as a function of temperature (experimental value)
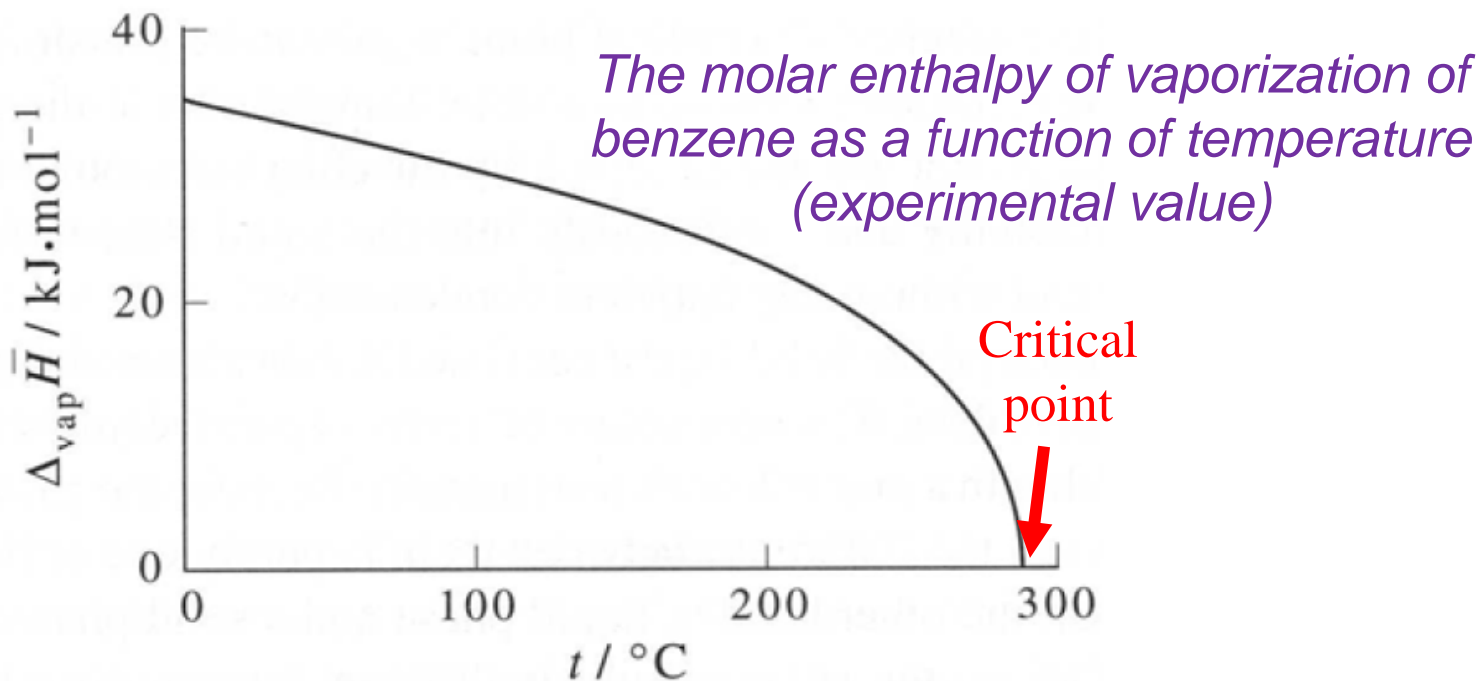
Critical point

- ✓ Looking at the vaporization enthalpy, it becomes 0 at the critical point.
- ✓ This is reasonable from the definition: $\Delta_{vap}H = T\Delta_{vap}S$. Because the two phases become less and less distinct as the critical point is approached, and finally merge into a single phase, $\Delta_{vap}S = S(gas) - S(liquid)$ should decrease and then be 0 at the critical point.
- ✓ There is no critical point between solid-liquid and solid-vapor (this textbook says they do not exist theoretically but maybe due to experimental difficulty)

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).

The phase diagram of water

The pressure dependence of the melting point of water
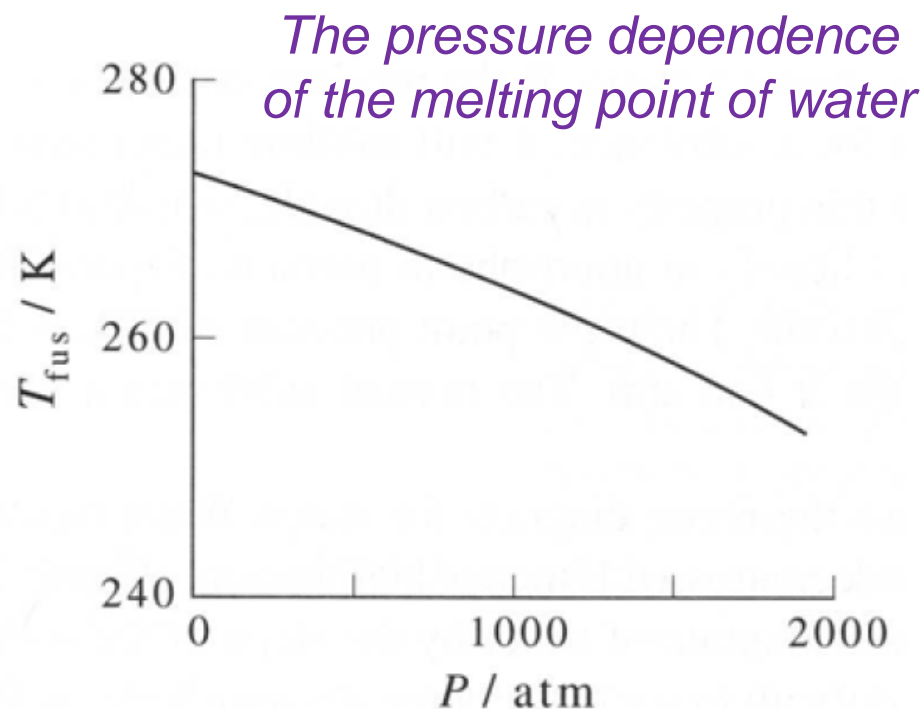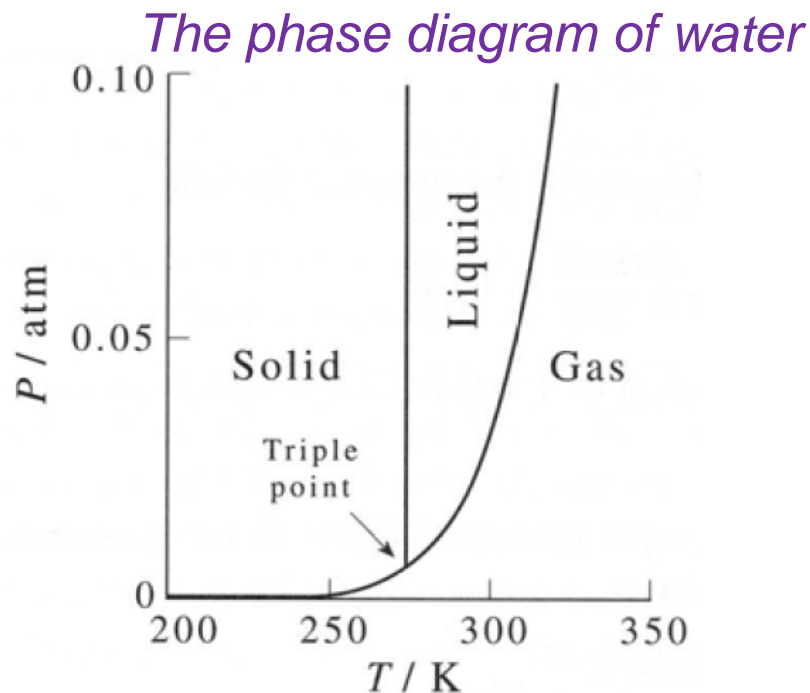
✓ Water has the unusual property that its melting point decreases with increasing pressure. (clearly seen in right figure)

✓ In the phase diagram, this unusual property is reflected as that the solid-liquid coexistence curve points upward to the left.

✓ This basically come from the fact that the molar volume of ice is greater than that of water under the same conditions. Antimony and bismuth show the same behavior; however most substances contract upon freezing.

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).
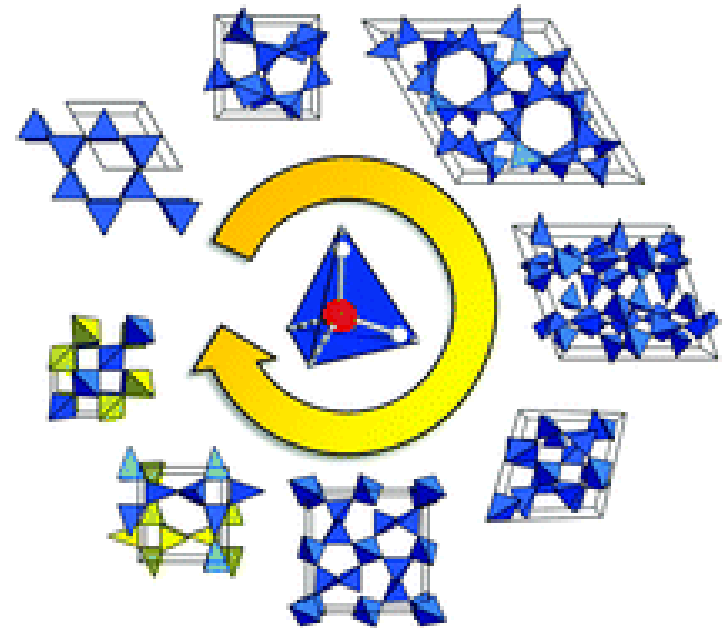
*The phase diagram of water at high pressures*
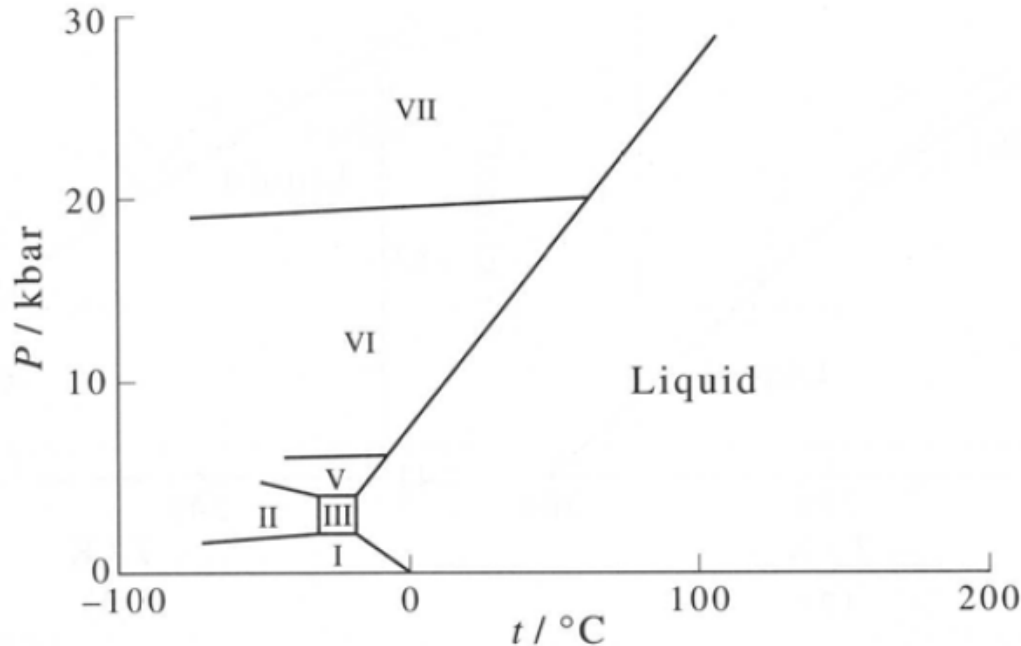
Various ice crystals

C.G. Salzmann et al., Phys. Chem. Chem. Phys., 2011,**13**, 18468-18480.

✓ Many substances exhibit a variety of solid phases (at high pressures).
✓ For example, solid water (namely ice) exhibit multiple structures. Ice (I) is the "normal" ice. These different structures are characterized by different symmetry of the crystal. As results, they have different molar enthalpy of formation and molar entropy.
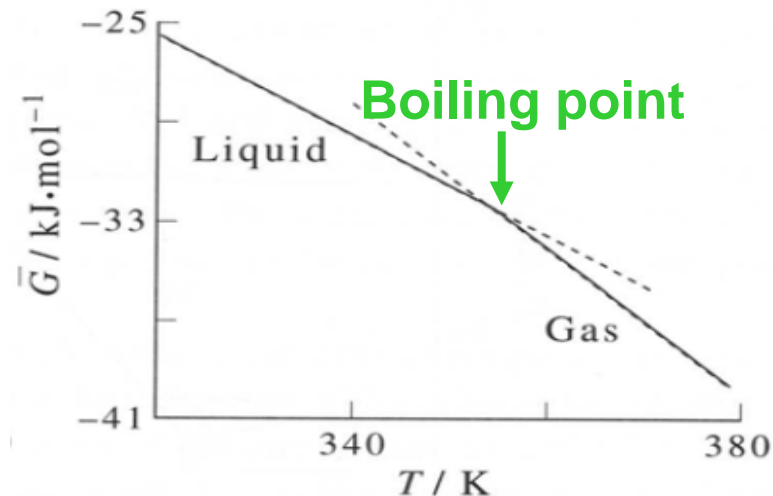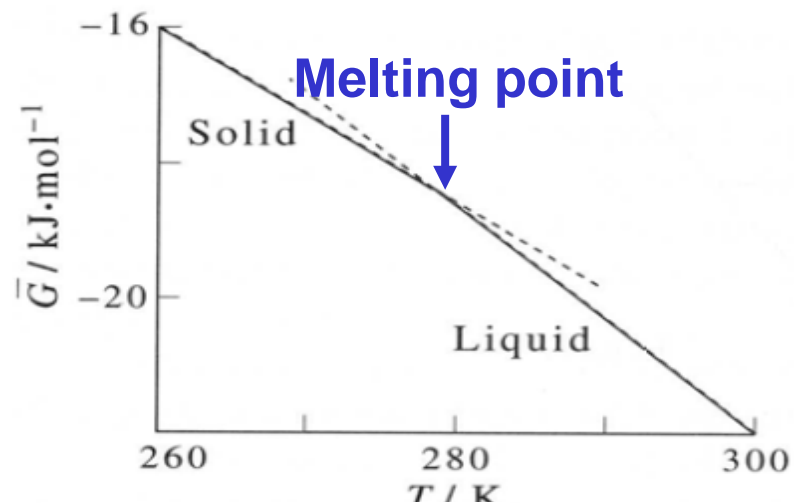
The phase diagram of benzene
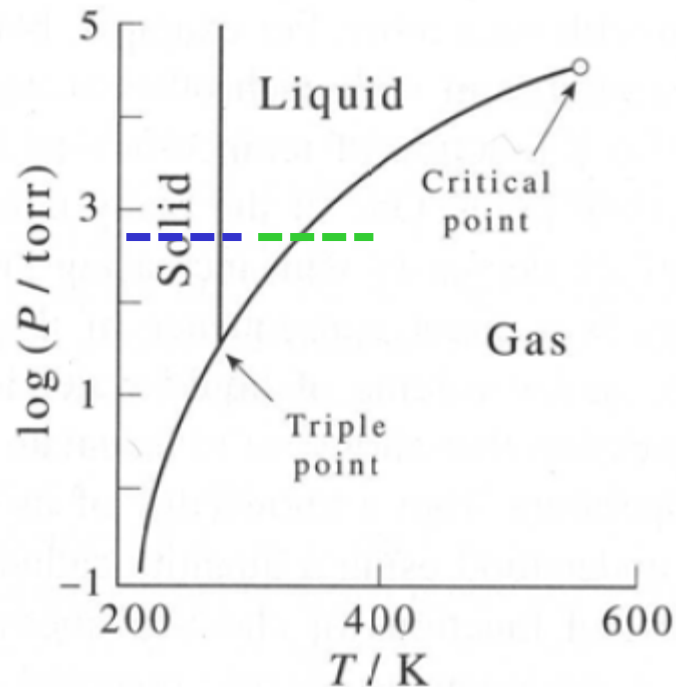
The molar Gibbs energies ($\bar{G}$) as a function of temperature at around phase transitions for benzene

Melting point

Boiling point

*D.A. McQuarrie, J.D. Simon, "Physical Chemistry: A Molecular Approach", University Science Books (1997).